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# Switching properties of Li-benzene complexes in a uniform electric field: a case where a "small" change makes a big difference.

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The effect of a homogeneous static electric field on the Li-benzene complex in two configurations, one with a larger Li-$C_6H_6$ distance ("loose") and one with a shorter distance ("tight") has been investigated. The electric field had the same orientation as the direction of the dipole moments of the complexes. When the direction of field intensity vector was the same as that of the dipole moment vector, optimization of the complex's geometry in one configuration resulted in switching it to the other one. Reversing the direction of the field then transformed the other configuration back to the original one. This switching behavior was observed beginning with the loose configuration and with the tight. The geometrical and electronic parameters of the complex after four steps of the reversible switching have been calculated for a selected field intensity of 0.005 atomic units (a.u.), that is 0.257 V/ Å.

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Molecular switches are molecules that can reversibly change between two states. The switching may be triggered by a variety of factors, such as pH, temperature, light, electric field, etc. A shift between the states of a molecular switch implies an abrupt change in its properties, which include geometric, optical, electric, and others. The most well known are pH indicators, which have been studied for a very long time, but the molecules or systems that have been most extensively investigated are those that undergo structural and optical transformation influenced by light, or, in a broader sense, electromagnetic radiation. Among these phototropic switches, one can mention azobenzenes,[1-5] spiropyrans,[6] diarylethylenes,[7-8] fulgides,[9] hexatrienes,[10] pyrene derivatives,[11-12] and salicylidene methylamine.[13] Of the switching potential of the chemical environment, apart from the well-known impact of pH on the absorption spectra of many dyes, one can also mention a newer example of switching: the tautomeric keto-enol equilibrium under acid addition.[14]

Reports concerning the impact of an electric field (EF) on the properties of isolated molecules are relatively scarce, although the effect of an EF on the isomer ratio of molecules[15] has been known for a long time. Another effect is the spatial separation of individual conformers of 3-aminophenol using inhomogeneous electric field.[16] The EF effect on the nature of chemical interaction was also investigated as properties of hydrogen bonds in complexes with acceptor water molecules.[17] One can also mention a theoretical paper devoted to the conformational behavior of chemisorbed azobenzene derivatives in an external EF.[18] Another theoretical investigation of a tautomeric system was found in which three tautomers and transition states between them were characterized in the EFs of varying strength. The relative energies of the three tautomeric forms changed linearly in response to varying EF strength and polarity.[19] Recently, a review devoted to perspectives on external electric fields in molecular simulation has appeared. Its main concern unlike the papers mentioned above, was for systems of technological importance and for biological structures.[20]

A genuine molecular switch should be reversible and able to go to many switching cycles without deterioration. Such switches have been found among those that react to the chemical environment or light.[10] We have found an example of a reversible switch triggered by the EF of proton-transfer in salicylidene aniline, the report of which was published recently.[21]

Investigations of molecular switches were prompted by expectations of them serving as circuit elements in molecular electronics and hence the rate of switching process has also been investigated in systems that display switching properties.[12,13, 21] These, and other molecular electronic devices, however, will probably be replaced by robust crystalline extended devices.[22] Apart from the possible application in electronics, the behavior of molecules in EFs is of a great interest to basic theoretical and experimental chemistry and biology. For example, it has been demonstrated that electric fields generated by cell membrane are more than sufficient to produce dissociation of molecular complexes as they approach within 8 nm of the membrane.[23] The authors state that it may be possible to apply electric dissociation in a specific manner for practical purposes such as drug delivery.

The aim of the present investigation was to find a molecule that would be sufficiently labile to be modified by an external uniform electric field and to check its properties in the field. The Li-$C_6H_6$ complex, chosen first, is a very interesting object because the interaction of Li atoms with benzene molecules provides an interesting model for the interaction of Li with aromatic systems, even in the intercalation compounds of Li with graphene. Its properties appeared quite unexpectedly. The application of an EF of a proper direction brought about a reversible switching behavior between two configurations of the complex. It was previously found that complexes of Li with benzene, and with a number of polycyclic aromatic hydrocarbons, can assume two configurations.[24-27] One configuration, of lower energy, was characterized by a greater Li-hydrocarbon distance and was named “loose”. In this configuration, the transfer of 0.1-0.3 electrons from benzene to the Li atom was detected, and the structure of the complexes could be represented as $Li^{\sigma-}\ldots C_6H_6^{\sigma+}$. In the second, “tight” configuration the distance was smaller and the opposite direction of charge transfer was determined. The first configuration was characterized by a planar geometry of the benzene ring, and the second by a boat geometry.[27] We expected a modification of their geometrical and electronic properties after exposure to the field.

All calculations were performed with the Gaussian 09 suite of programs.[28] The complexes’ geometry and normal vibrations were calculated at the MP2 level with the 6-311++G** basis set, with and without an uniform external EF. The EF was included in the calculations using the options available in Gaussian09, as was the spatial integration of electron density. Strength of the external electric field (E) ranged from 0.001 to 0.005 a.u., that is 0.0514 to 0.257 V/Å. In Cartesian coordinates, the Li atom in the complexes lies along one axis at points more positive than the coordinates of the benzene center. The axis is a symmetry axis of the complex. The dipole moment in Gaussian is reported from negative to positive as the positive direction. The complex in which there is a charge transfer from benzene to the Li atom is therefore characterized by a negative dipole moment, whereas a positive dipole moment indicates the opposite direction of charge transfer. Concerning the applied external EF, its vector was set parallel to the symmetry axis of the complexes. The sign of its intensity, E, according to Gaussian convention, is defined from the negative plate to the positive. For example, when the negative field is applied to a loose complex, which has a negative dipole moment along the symmetry axis, the two vectors will be parallel and have the same orientation.

***The loose complex.*** Dipole moment of the complex was calculated as a function of E, while the EF was directed from the Li atom to the benzene center (Fig.1a). For the weakest fields, – 0.001 to – 0.003 a.u., the negative dipole moment of the complex diminished, but at stronger fields, near -0.004 a.u., the dipole moment abruptly changed sign (to 4.5 Debye at E = – 0.005 a.u.). Taking in mind that the positive dipole moment characterized the tight complex we expected that EF of this direction and sufficient intensity would cause the loose complex to switch to the tight one. To answer the question, the geometry of the molecule was determined after applying an EF of intensity of -0.005 a.u. to the initial molecule. It appeared that the ring geometry changed from planar to boat. This transformation was named “step 1” in Table 1. It was interesting to see whether the switching was reversible or not. An electric field of the opposite sense (+0.005 a.u.) was applied to the molecule obtained in step 1; this transformation was named step -1. The action was successively repeated in a similar manner, described as step 2 and step -2. In every case, a field opposite to that of the preceding step was applied. The data in Table 1 show that it was possible to transfer one complex (loose or tight) to the other one by applying an EF of the proper sense, and that the application of an EF was reversible. This interesting result prompted us to see what would be the effect of applying an EF to the tight complex.

***The tight complex.*** The plot of the dipole moment as a function of positive E is given in Fig.1b. This time, the direction of the EF was from the benzene center to the Li atom. For the weakest fields, the positive dipole moment of the complex diminished, but in the field between 0.001 and 002 a.u. the dipole moment abruptly changed sign. The same cycle of four steps of optimization in the positive and negative EF were performed for the tight complex, as it was for the loose complex. The results are shown in Table 2. It can be seen that starting from the tight configuration, we also obtained a series of configuration switches, similar to that found for the loose complex presented in Table 1.

It can be seen that in this case, application of the electric field is also reversible; the same molecule is obtained after steps 1 as after step 2, and after step -1 as after step -2. Optimization of the latter, after removing the field, generated the same molecule as the initial one. Switching between the two configurations of the Li-$C_6H_6$ complex in a homogeneous electric field is represented in Fig.2.

**Comparison of the strengths of the internal and external electric fields.** The most unexpected finding was that made by comparing the intensity of applied EF with that of the intrinsic field within the molecules. Let us compare the fields along the symmetry axes of the complexes, passing through the Li atom and the centroid of benzene molecule. In the case of the loose complex, the intensity of its original intrinsic field runs from – 0.0159 a.u. in the centroid of benzene ring to – 18.536 a.u. at a 0.2 Å distance from the Li atom. The applied field, 0.005 a.u., was about 3 times weaker in the center of benzene ring, and 3,707 times weaker at 0.2 Å from the Li atom. The corresponding factors for the tight complex are 8.5 and 3,269, respectively. At the halfway point between the Li atom and the benzene ring centroid, the intrinsic field strength (no-field case) was 28.5 times greater than that of the applied field of 0.005 a.u. (for the loose complex) and 73 times greater (for the tight complex). Fig.3 shows a comparison of the total field along the axis of the loose complex while in an external EF of intensity 0.005 a.u. to the intrinsic field before applying the external field. It can be seen that the difference in the field intensity is scarcely perceptible. Nevertheless, the radical reorientation of the electron density and modification of the complexes' geometry do occur.

## Conclusions

**-** In the absence of an applied EF, two configurations of the complex can be optimized, the tight configuration being of higher energy: 0.19 eV at the MP2/6-311++G** level.

- In an applied EF of appropriate direction, a reversible switching between the two configurations took place. For both configurations, this direction has the same orientation as the vector of the molecular dipole moment.

- The switching cycles were tracked with an applied field EF of 0.005 a.u. intensity. Comparison of that value with the intensity of the internal EF in the no-external EF case showed that the latter, at a point halfway between the Li atom and the benzene ring centroid is many times larger than the external field (28.5 and 73, in the loose and tight complex, respectively).

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## Figures captions

Figure 1. Plots of dipole moment value and direction of the Li-$C_6H_6$ complex as a function of intensity of the applied electric field: (a) – Complex in the loose configuration, (b) – Complex in the tight configuration.

Figure 2. Two configurations of the Li-$C_6H_6$ complex and their dipole moment. The external electric field of the direction shown by arrows switches the first configuration to the second.

Figure 3. The internal electric field along the symmetry axis in the loose configuration ( | ) and the total field in the configuration while subject to an external field of intensity 0.005 a.u.(| ).

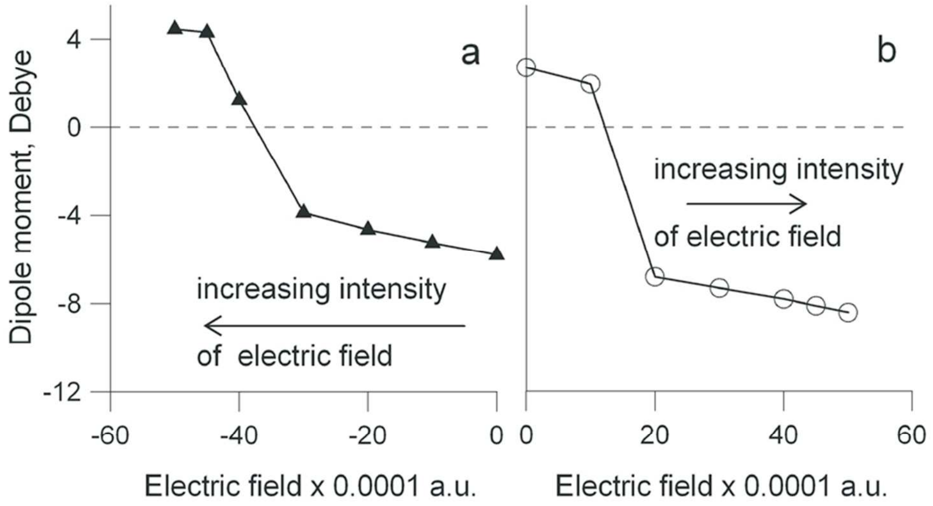
Table 1. Dipole moment, energy, and geometrical parameters of the loose Li-$C_6H_6$ complex influenced by an electric field of negative direction (steps 1 and 2) and positive direction (steps -1 and -2) with respect to the complex symmetry axis.

| Configu-ration | Field intensity, a.u. | Dipole moment, Debye | Distance Li-centroid of benzene ring*, Å | Max dihedral angle in benzene ring, deg | Energy, hartree | Energy difference to initial configu-ration,eV |
|---|---|---|---|---|---|---|
| Initial | 0 | -5.8 | 2.241 | 0.03 | -239.02406 | |
| Step 1 | -0.005 | 4.5 | 1.813 | 16.5 | -239.02410 | -0.001 |
| Step -1 | +0.005 | -8.4 | 2.119 | 0.00 | -239.03795 | -0.378 |
| Step 2 | -0.005 | 4.5 | 1.814 | 16.6 | -239.02410 | -0.001 |
| Step -2 | +0.005 | -8.4 | 2.119 | 0.00 | -239.03795 | -0.378 |

*measured as a distance from the Li atom to the centroid of benzene ring (for the loose, nearly planar complexes) or as a distance from the Li atom to the plane of the four coplanar carbon atoms of benzene ring (for the tight, boat-like complexes).

Table 2. Dipole moment, energy, and geometrical parameters of the tight Li-$C_6H_6$ complex influenced by an electric field of positive direction (steps 1 and 2) and of negative direction (steps -1 and -2) with respect to the complex symmetry axis.

| Configu-ration | Field intensity, a.u. | Dipole moment, Debye | Distance Li-centroid of benzene ring, Å | Max dihedral angle in benzene ring deg | Energy, Hartree | Energy difference to initial configu-ration,eV |
|---|---|---|---|---|---|---|
| Initial | 0 | 2.6 | 1.801 | 16.5 | -239.01693 | |
| Step 1 | +0.005 | -8.4 | 2.121 | 0.0 | -239.03791 | -0.571 |
| Step -1 | -0.005 | 4.4 | 1.814 | 16.6 | -239.02410 | -0.195 |
| Step 2, | +0.005 | -8.4 | 2.119 | 0.0 | -239.03791 | -0.572 |
| Step -2 | -0.005 | 4.5 | 1.814 | 17.7 | -239.02410 | -0.195 |



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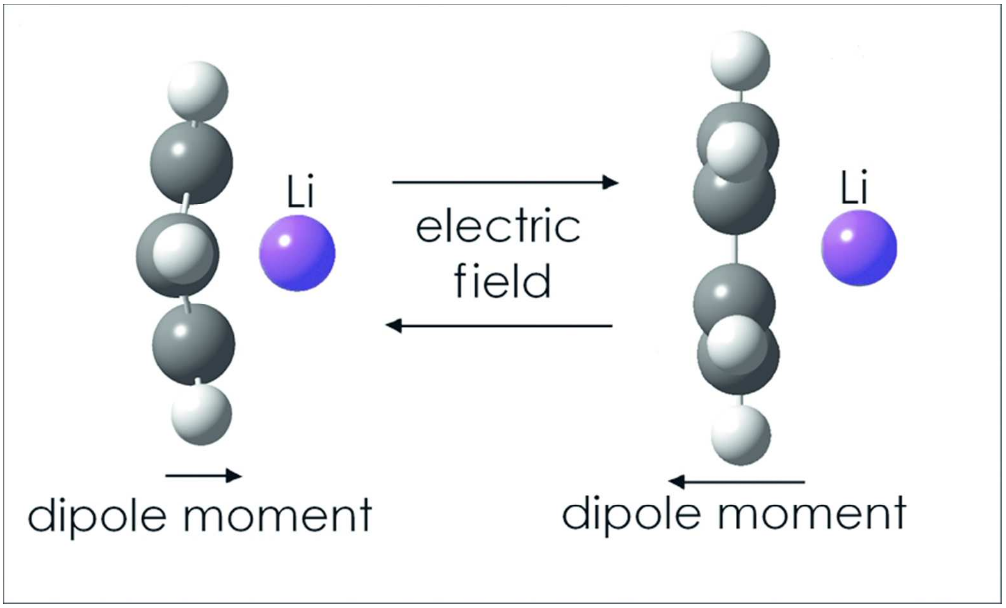

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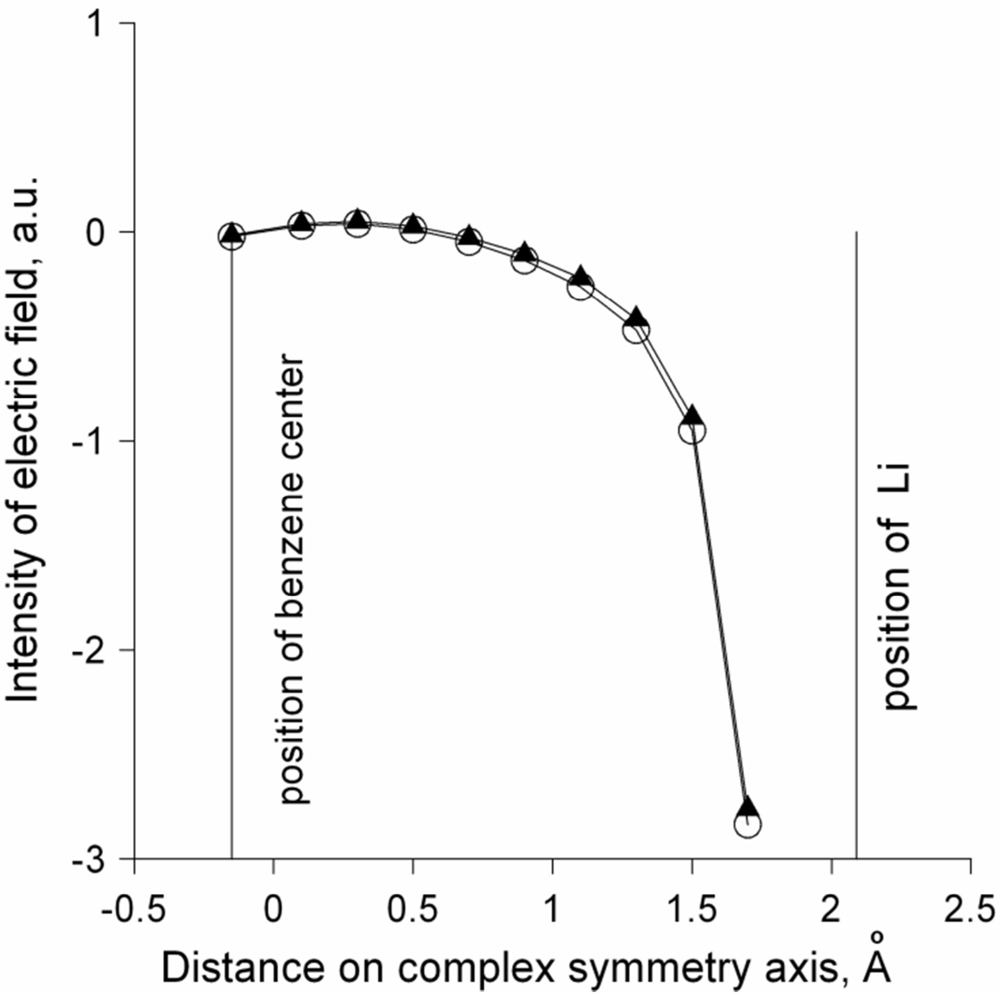

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